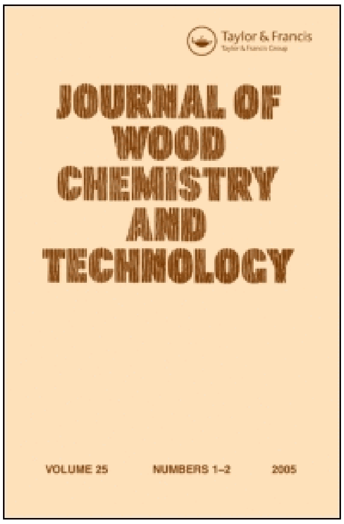

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Graft Copolymerization of Furfuryl Alcohol and Cellulosic Materials

Chieu Nguyen[a]; Eugene Zavarin[a]
[a] University of California, Forest Products Laboratory, Richmond, California

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GRAFT COPOLYMERIZATION OF FURFURYL ALCOHOL AND CELLULOSIC MATERIALS

Chieu Nguyen and Eugene Zavarin
University of California
Forest Products Laboratory
Richmond, California

ABSTRACT

Furfuryl alcohol (FA) in aqueous medium at pH 2.0 and 90°C in presence of H_2O_2/Fe^2 polymerized under crosslinking, without grafting to cellulosic fibers if present. Under the same conditions acid-prepolymerized furfuryl alcohol (PFA) transformed into a water-soluble polymer that grafted to cellulosic fibers (polymer load of 68%) with a negligible formation of a crosslinked homopolymer. Decrease in the reaction temperature or increase in the volume of water decreased the polymer load and grafting efficiency. Increases in the concentrations of H_2O_2, of Fe^{2+}, of both, or of pH resulted in curves exhibiting maxima in grafting efficiency and polymer load. This was explained by the presence of second and first order members in the equation for the reaction rate of the formation of grafting active centers on PFA or cellulose. Increase in cellulose consistency decreased the polymer load but influenced the grafting efficiency to a secondary extent only, suggesting that activation of PFA rather than that of cellulose is responsible for grafting. Pretreatment of cellulose with H_2O_2/Fe^{2+} before addition of PFA resulted in no grafting. Pretreatment of PFA before addition of cellulose gave a polymer load amounting to about 40% of what would have been expected if both reaction partners had been reacted simultaneously. This was explained by formation of time-stable active centers on PFA and of time-unstable active centers on PFA or cellulose.

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INTRODUCTION

The conventional methods for wood bonding are generally based on the use of phenol-formaldehyde and urea-formaldehyde adhesives and exhibit several disadvantages including availability and cost of raw materials and emission of the toxic formaldehyde and phenol during manufacture and use of the glued products. In recent years this prompted studies of alternative methods of bonding.[1] One of such methods makes use of furfuryl alcohol in a mixture with lignosulfonates and maleic anhydride. In the presence of oxidants such as hydrogen peroxide or nitric acid usually sprayed on wood, this mixture reacts at elevated temperatures in a press and bonds the wood surfaces to each other.[2-5] It was thought that the processes responsible for this bonding bear resemblance to what takes place in grafting of organic monomers to lignocellulosic materials, and involve polymerization of furfuryl alcohol and its grafting to the lignocellulosic backbone.[6]

Furfuryl alcohol is a furan type reactive compound commercially made by reduction of furfural, with the latter produced from agricultural residues. In acidic media furfuryl alcohol polymerizes readily by condensation with formation of chains of furyl units joined by methylene groups. The polymers may include also some difurfurylether linkages, as well as some 1,4-diketo structures[7] resulting from hydrolytic ring opening. Occasionally, during condensation the methylol side chains split under formation of formaldehyde, which can condense in turn with the polymer.

In contrast to the ready acid polymerization, no reports are available on successful oxidative polymerization of furfuryl alcohol, except for a preliminary study by Philippou[6] who reported polymerization of furfuryl alcohol with hydrogen peroxide at 90°C and observed differences between acid and hydrogen peroxide polymerizations in Differential Scanning Calorimetry (DCS), as well as differences in IR and UV spectra of the products. Philippou assumed that polymerization of furfuryl alcohol in presence of hydrogen peroxide proceeds by a free radical pathway. The idea of Philippou is contradicted, however, by the experiments of Gandini and Rieumont,[8] who studied the reaction of azo-bis-isobutyronitrile as a radical initiator with various furan derivatives including furan, 2-methylfuran, ethyl-2-furoate, and 2-furaldehyde. The reaction products were derivatives of dihydrofuran or its dimer, formed by addition of a free radical to the double bond of the furan ring. No higher oligomers or polymers could be identified. The results suggest that furan units <u>per se</u> are unable to undergo oxidative chain polymerization by the free radical mechanism. At the same time it was conclusively demonstrated that polymers including alternating furan or 2-methylfuran and maleic anhydride derived units could be synthesized by a free radical mechanism.[9-11] The polymerization of vinyl acetate and dimethyl fumarate leading to structures with alternating units rather than to structures with randomly distributed units has recently been explained in terms of frontier orbital interactions.[12]

While extensive work has been done on grafting various vinyl monomers such as methylmethacrylate, acrylonitrile, styrene, and methylacrylamide to cellulose using one-electron oxidants such as hydrogen peroxide/ferrous ion, ceric salts, organic peroxides, or electromagnetic radiation, very little is known on grafting furfuryl alcohol or its acid polymer. Apparently the only report available is that of Philippou,[6] mentioned before, who described grafting of furfuryl alcohol and furfuryl alcohol/ammonium lignosulfonate mixtures to wood particles using hydrogen peroxide (without added Fe^{2+}) as a free radical generating oxidant and reported polymer loads of up to 9.39% and 11.18%, respectively. In this paper we report the results of experiments on grafting furfuryl alcohol and its acid-polymer to cellulosic fibers using hydrogen peroxide/ferrous ammonium sulfate as activator. It was envisaged that such experimentation might shed some light on the bonding processes mentioned previously. While the results strongly suggest that acid-polymerized furfuryl alcohol can be efficiently grafted to cellulose with H_2O_2/Fe^{2+}, the final proof by isolation of the linked polymer units is reserved for the future.

RESULTS AND DISCUSSION

Solubility of Homopolymers

To determine polymer load and grafting efficiency the grafted product must be separated from the homopolymers formed as a side product during the grafting reaction. In cases where homopolymer represents linear molecular chains the separation can be commonly accomplished by extraction of the reaction product with a suitable solvent. In other cases, where the homopolymer represents a three dimensional, crosslinked material, the separation problem becomes much more involved if not impossible. In our work we were confronted with both types of homopolymer side-products: the linear polymer of furfuryl alcohol (PFA) formed during the grafting reaction by acid condensation of furfuryl alcohol (FA) when FA was used in grafting; more often, however, commercial PFA (Quacorr 1300) was used directly as a component of the grafting mixture. The cross-linked polymer formed on heating FA or PFA at a low pH in presence of H_2O_2/Fe^{2+} for extended time periods.

To find the suitable solvent for extraction of the free PFA (either initially added or formed during the reaction) twenty odd liquids of various solubility parameters and hydrogen bonding properties were examined. At ambient temperature commercial PFA (Quacorr 1300) was only partially soluble in any of the solvents tested at 1:1 solvent to PFA ratio; PFA was completely soluble in N-methyl-2-pyrrolidone at $\geqslant$ 3:2 solvent to PFA ratios and in tetrahydrofuran, acetone, dioxane, and furfural at $\geqslant$ 7:3 ratios. All these solvents are poor proton donors, but relatively good proton acceptors with solubility parameters ranging from 9.1 to 11.3 $[cal/cm^3]^{1/2}$. For practical reasons it was decided to use acetone for extraction.

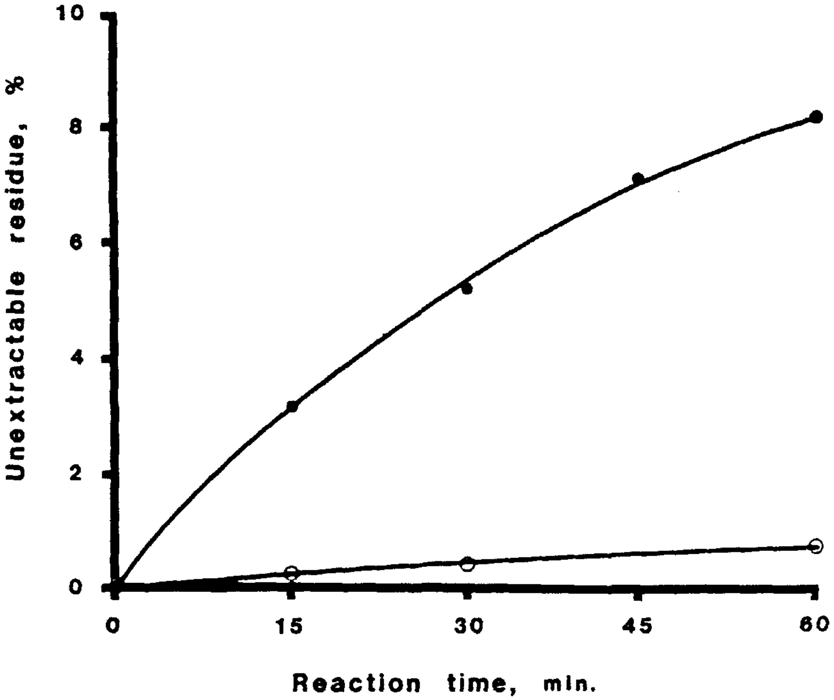


FIGURE 1. Influence of reaction time on the crosslinking of FA (black circles) and PFA (white circles). Reaction conditions: pH = 2.0; Temp. = 90°C; Fe^{2+} = 0.01 x 10^{-3} mole; H_2O_2 = 35.0 x 10^{-3} mole; FA or PFA = 2.5 g; Total aqueous volume = 100 ml.

The rate of formation of the crosslinked PFA was examined at pH = 2.0 at 90°C in aqueous medium. Heating of either FA or PFA (Quacorr 1300) for 2 hours in absence of oxidants did not result in any crosslinking with the resulting polymers remaining soluble in acetone. In presence of H_2O_2 and catalytic amount of Fe^{2+}, both FA and PFA gave the products that could be separated into three fractions: A) Acetone soluble, water insoluble material, essentially identical with PFA; B) water soluble, acetone insoluble

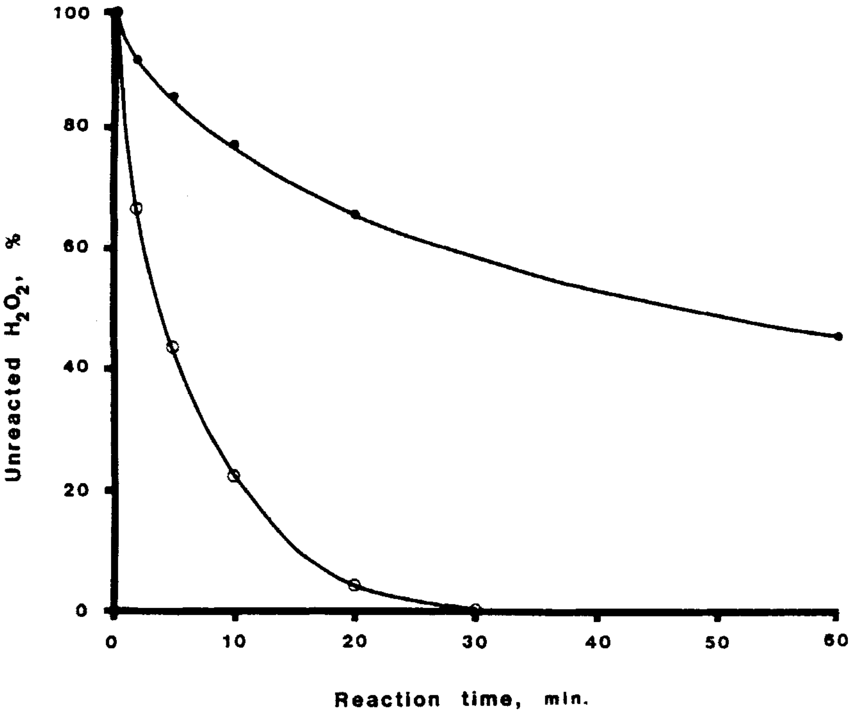


FIGURE 2. H_2O_2 usage in PFA/cellulose (black circles) and FA/cellulose (white circles) grafting reactions. Reaction conditions were as listed in Table 1, except Fe^{2+} = 0.01 x 10^{-3} mole.

material; and C) acetone and water insoluble (crosslinked) material. The amount of the insoluble, crosslinked material gradually increased with time (Figure 1), and amounted up to 8.4% in case of FA and 0.8% in case of PFA (Quacorr 1300) after one hour heating. The difference in the rate of formation of the crosslinked material is most likely connected with the solubility of FA and its oligomers in the aqueous reaction medium (while PFA is initially practically insoluble) and the resulting increased ability to react with H_2O_2/Fe^{2+} followed by crosslinking.

TABLE I.

Rate of Hydrogen Peroxide Usage in Presence of FA, PFA, Cellulose, and Other Pertinent Organics.

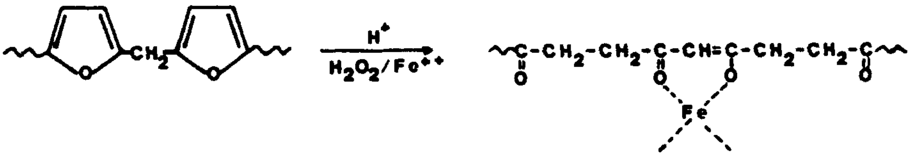
Organic Mixture*	Time to 90% Hydrogen Peroxide Usage (minutes)	Concentration of the Alcoholic Monomers Added (Moles/Liter)
None	4.5	----
PFA	15.5	----
Cellulose	< 2.0	----
PFA/Cellulose	17.5	----
Cellulose + FA	< 2.0	0.26
PFA/Cellulose + FA	< 2.0	0.26
PFA/Cellulose + FA	< 2.0	0.06
PFA/Cellulose + n-Propanol	5.5	0.26
PFA/Cellulose + Benzyl Alcohol	< 2.2	0.26
PFA/Cellulose + Ethylene Glycol	7.2	0.09

*Conditions: Temp. = 90°C; pH = 2.0; aqueous phase = 100 ml; cellulose = 0.5 g; FA or PFA = 2.5 g; H_2O_2 = 35.0 x 10^{-3} mole; Fe^{2+} = 0.1 x 10^{-3} mole.

Subjecting cellulose fibers to the action of H_2O_2/Fe^{2+} for 1 hour at the conditions described resulted in weight losses of < 3.0%. These losses could be neglected in most calculations of polymer load and grafting efficiency and were most likely even less in grafting reactions due to attachment of the grafted chains to cellulose.

The Rate of Hydrogen Peroxide Usage

The decrease in H_2O_2 concentration in presence of a constant concentration of Fe^{2+}, alone or in combination with cellulose, FA, PFA, or other pertinent organics was studied as a function of time. The reaction conditions and results are summarized in Figure 2 and Table 1. Addition of cellulose or cellulose-FA mixture speeded up, while addition of PFA or cellulose-PFA mixture considerably slowed down the H_2O_2 usage. Two explanations could be advanced for that. According to one the catalytically acting Fe^{2+} or more likely Fe^{3+} formed during the reaction could be partially or fully removed from the reaction medium by some chelating groups present in PFA, such as β-diketo groups; the latter can be formed by acid hydrolysis of the neighboring furyl rings (reaction 1).[7] Chelation of Fe^{2+} or of Fe^{3+} by β-diketones is well known.[13]



The second explanation could be advanced assuming the following mechanism for the H_2O_2/Fe^{2+} oxidations:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\cdot \qquad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\cdot + H^+ \qquad (3)$$

$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \qquad (4)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+ \qquad (5)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^- \qquad (6)$$

$$HO^{\cdot} + HO_2^{\cdot} \rightarrow H_2O + O_2 \qquad (7)$$

$$HO. + RCH_2OH \rightarrow R\dot{C}HOH + H_2O \qquad (8)$$

$$Fe^{3+} + RCH_2OH \rightarrow Fe^{2+} + R\dot{C}HOH + H^+ \qquad (9)$$

$$Fe^{3+} + R\dot{C}HOH \rightarrow Fe^{2+} + RCH{=}O + H^+ \qquad (10)$$

With the reaction (2) fast, reaction (3) slow, and with reaction (8) about 50 to 150 times faster than reaction (4) in case of primary and secondary alcohols,[14,15] the rate of H_2O_2 consumption should depend upon the rates of reactions (9) and (10), both involving oxidation of organics by Fe^{3+} which leads to the formation of Fe^{2+}. Thus, the availability of organic groups able to reduce Fe^{3+}, such as RCH_2OH, should strongly influence the rate of H_2O_2 consumption. With cellulose macromolecules containing one RCH_2OH and two R_2CHOH groups per repeat unit and with PFA containing only one RCH_2OH group per chain (according to the data of the manufacturer - about one hydroxyl per 5 repeat units), cellulose would be expected to reduce Fe^{3+} much faster and lead to a faster H_2O_2 consumption than PFA, in agreement with what was found.[16] The slow rate of H_2O_2 consumption in case of PFA/cellulose mixture could be explained by the protection of cellulosic fibers from oxidation by PFA occlusion.

In order to evaluate the relative importance of the two alternatives, the concentration of free Fe^{3+} in aqueous solutions in presence of either cellulose or PFA (pH=2.0, Fe^{3+} = 0.1×10^{-3} mole,

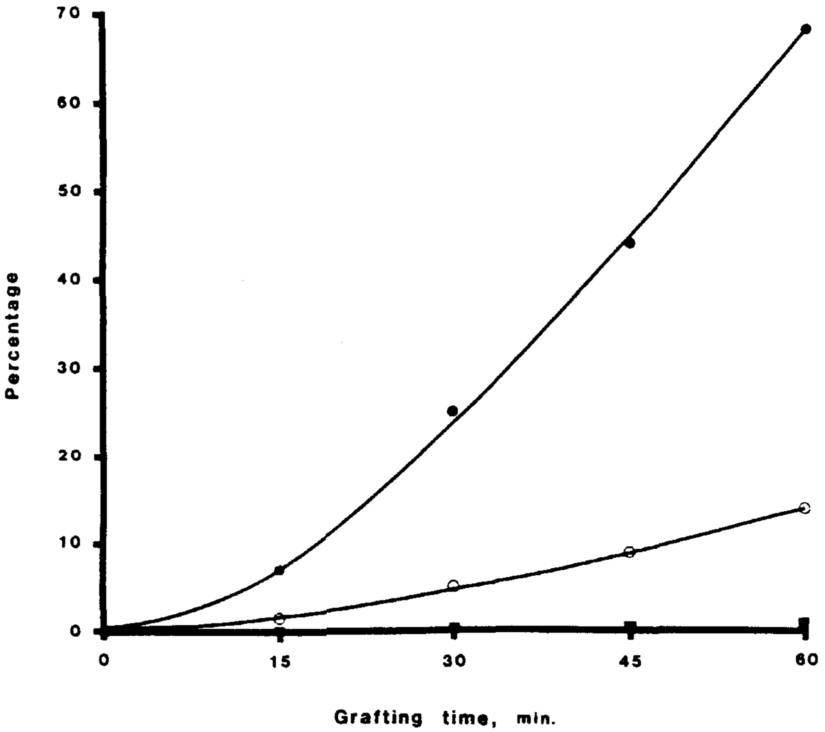


FIGURE 3. Effect of reaction time on grafting parameters in PFA-to-cellulose grafting. Black circles : polymer load (%); white circles : grafting efficiency (%); black squares : crosslinked PFA homopolymer (in % of PFA used). Reaction conditions as in Figure 1, cellulose = 0.5 g.

aqueous volume = 100 ml, T = 90°C) was determined colorimetrically. While cellulose adsorbed practically no Fe^{3+} after 2 minutes of heating, PFA adsorbed 69.4% of Fe^{3+} after the same length of time. In another set of experiments the effect of addition of water-soluble alcohols on the rate of H_2O_2 consumption in presence of PFA/cellulose was studied. In all cases, but particularly with more reactive furfuryl and benzyl alcohols, the rates increased substantially (Table 1). It was concluded that while chelation of Fe^{3+} by PFA could to some extent influence the rate of the oxidation reaction,[17] it is

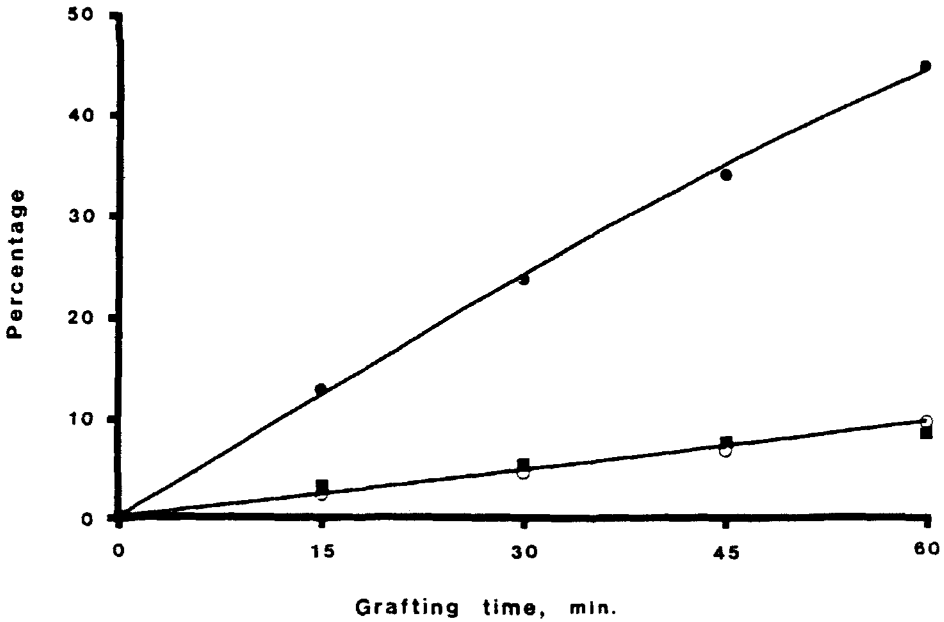


FIGURE 4. Effect of reaction time on grafting parameters in FA-to-cellulose grafting. Symbols and reaction conditions are as in Figure 3.

the availability and reactivity of R_2CHOH and RCH_2OH groups reducing Fe^{3+} to Fe^{2+} which is mainly responsible for the variations in the rate of H_2O_2 consumption.

Influence of Reaction Time on Polymer Load and Grafting Efficiency

The results of grafting FA and PFA to cellulose in presence of H_2O_2/Fe^{2+} are given in Figures 3 and 4. In absence of the oxidant very little or no grafting took place and the homopolymer could be completely separated from cellulose by acetone extraction.

In the presence of oxidant and using PFA as a grafting partner the cellulosic fibers remained dark brown after extraction with acetone and hot water, and their weight increased up to 168%. Since the insolubilization of PFA due to crosslinking in the reaction of PFA with oxidant is negligibly small (Figure 1), the weight gain should be attributed entirely to grafting. Assuming that oxidative activation of the polymers precedes the grafting step, the increase in grafting with time is most likely due to the rate of activation being of the similar magnitude as the rate of grafting (kinetics of successive reactions).

In the presence of oxidant, but using FA, the weight of cellulose fibers increased to 144.7% after acetone and hot water extractions and the rate of weight gain decreased slightly with time, as in the case of FA-crosslinking (Figure 1). The level of apparent grafting efficiency, i.e. the percent of PFA that became acetone and hot water insoluble was also close to that obtained in the absence of cellulose (Figure 4). This casted doubt as to whether any grafting took place in this case at all.

In order to clarify this point the FA-H_2O_2/Fe^{2+} polymerization reaction was run in absence and in presence of cellulose, and the reaction products as well as unreacted cellulose fibers were acetylated and treated with CH_2Cl_2/methanol, 9:1.[18] The results are summarized in Table 2. Acetylated cellulose completely dissolved in the above solvent, while crosslinked PFA was completely insoluble, gaining even some weight due to the introduction of acetyl groups. This weight gain was appreciably less with the material subjected to the longer oxidation time suggesting gradual loss of hydroxyls in crosslinking.

The grafted cellulose samples were found to be largely, but incompletely soluble in the mentioned solvent. The weight of the insoluble part agreed reasonably well with the figures for polymer load after correction for the introduced acetyl groups, suggesting that the insolubles were composed predominantly of cellulose-free

TABLE II.

Solubility of Acetylated and of Hydrolyzed Crosslink and Graft Polymers***

Polymer	Percent of Acetylated Polymers Insoluble in CH_2Cl_2/CH_3OH, 9:1 Not Corrected for Acetyls (%)	Percent of Acetylated Polymers Insoluble in CH_2Cl_2/CH_3OH, 9:1 Corrected for Acetyls (%)	Percent of Acetylated Polymers Insoluble in H_2SO_4 Hydrolysis Medium	Polymer Load (%)	Percent of Crosslinked Polymer Formed in Absence of Cellulose
Crosslinked PFA** (60 min. reaction time)	106.9	100.0	----	----	----
Crosslinked PFA** (30 min. reaction time)	113.0	100.0	----	----	----
FA Grafted Cellulose* (60 min. grafting)	49.6	45.2	42.3	44.4	41.0
FA Grafted Cellulose* (45 min. grafting)	35.4	34.4	31.4	33.3	35.8
FA Grafted Cellulose* (30 min. grafting)	25.3	25.0	22.1	23.3	26.1
FA Grafted Cellulose* (15 min. grafting)	16.8	15.5	13.3	13.0	16.2

*The figures (including last column) are expressed in percent based on the weight of original cellulose fibers as 100%.

**No PFA dissolved and the filtrate was clear. The increase in weight is due to the introduced acetyl groups; these figures were used to correct the last four figures of column two.

***The conditions were the same as given in Figure 4. Acetylated cellulose fibers dissolved completely in CH_2Cl_2/CH_3OH, 9:1 solvent.

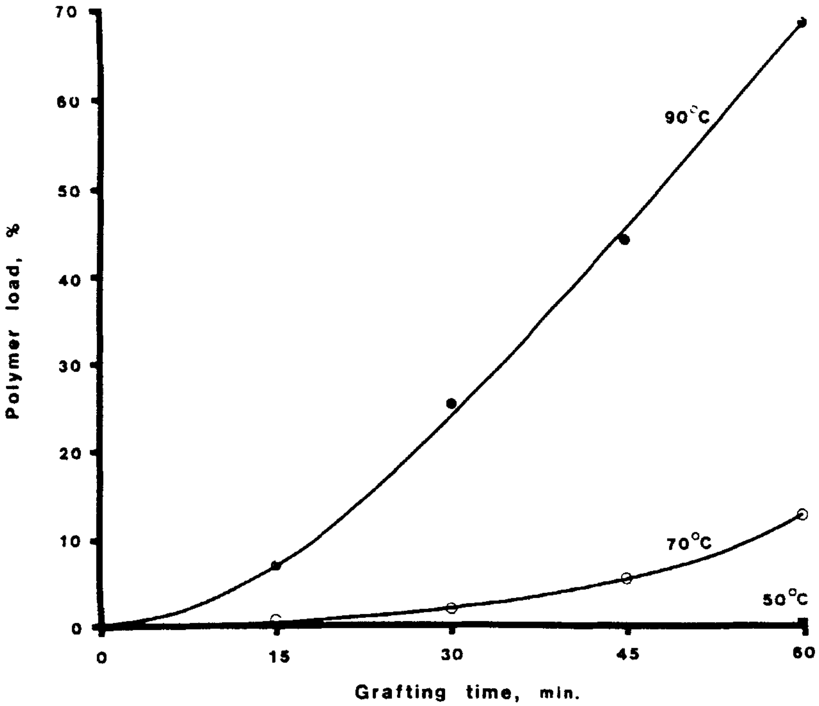


FIGURE 5. Effect of temperature and reaction time on polymer load in grafting PFA to cellulose. Reaction conditions are as in Figure 3.

crosslinked PFA. To further substantiate this the acetylated insolubles were subjected to acid hydrolysis under conditions conducive to a complete cellulose hydrolysis.[19] The insoluble hydrolysis residues exhibited only small weight losses which could be largely explained by the splitting of acetyl groups, with the figures only slightly below the figures for polymer load and for acetyl-corrected CH_2Cl_2/CH_3OH insolubles. The small difference could well be due to the loss of water in condensation reactions taking place during acid hydrolysis.

The experiments thus suggest that only negligible amount of grafting takes place with FA, with the bulk of FA transforming into oxidatively crosslinked PFA without grafting. This could be due to the water solubility of FA and its oligomers and a greater possibility to interact with H_2O_2/Fe^{2+}, followed by crosslinking in aqueous medium, away from cellulose. Additional factors could be connected with the difference in molecular weight of the grafted chains, and the difference in the number of reactive sites within the polymer chains.

Influence of Reaction Temperature on Polymer Load and Grafting Efficiency

Results of grafting of PFA to cellulose at 50°, 70°, and 90°C are summarized in Figure 5. The polymer loads increase strongly with temperature. While this could be explained simply by increases in the rates of PFA chain attachment to the cellulose backbone, in reality the relationships are likely to be more complicated and the magnitude of the polymer loads should also depend upon changes in solubility of PFA in aqueous medium, on changes in the rate of acidic chain extension of PFA, on changes in the rates of oxidative activation processes, as well as on other factors.

Influence of Concentration of H_2O_2 and of Fe^{2+} on Polymer Load and Grafting Efficiency

With PFA grafting the increase in H_2O_2 concentration, the increase in Fe^{2+} concentration, and the increase in the concentration of H_2O_2/Fe^{2+} oxidant (both constituents held in a constant ratio), sharply increased the polymer load and grafting efficiency up to a well defined maximum; further increase in H_2O_2, Fe^{2+}, or H_2O_2/Fe^{2+} resulted in a gradual decrease in both polymer load and grafting efficiency (Figures 6-8).

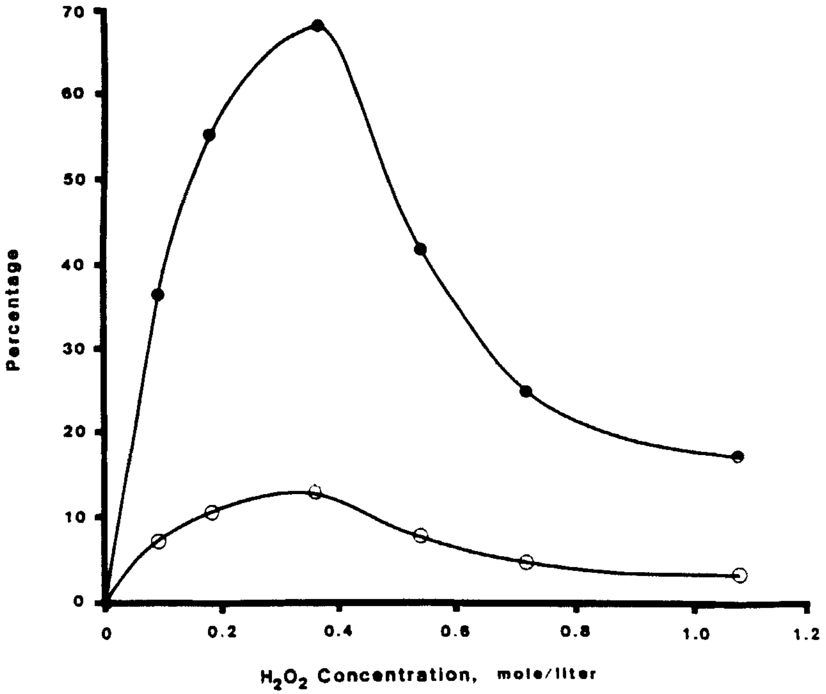


FIGURE 6. Effect of H_2O_2 concentration on polymer load, % (black circles) and grafting efficiency, % (white circles) in grafting of PFA to cellulose. Reaction conditions are as in Figure 3.

Assuming that grafting takes place through formation of active centers (A.C.) in cellulose or in PFA through reaction with hydroxyl radicals followed by the reaction of such centers with nonactivated portions of the grafting partner, the polymer load and grafting efficiency should depend upon the concentration of such active centers (reactions 2,8,9,10). The concentration of active centers should depend in turn upon the rate of formation of such centers by the reaction of the material to be activated with hydroxyl radicals (k_f) on one hand (i.e. upon concentrations of H_2O_2 and Fe^{2+}), and upon the disappearance of such centers

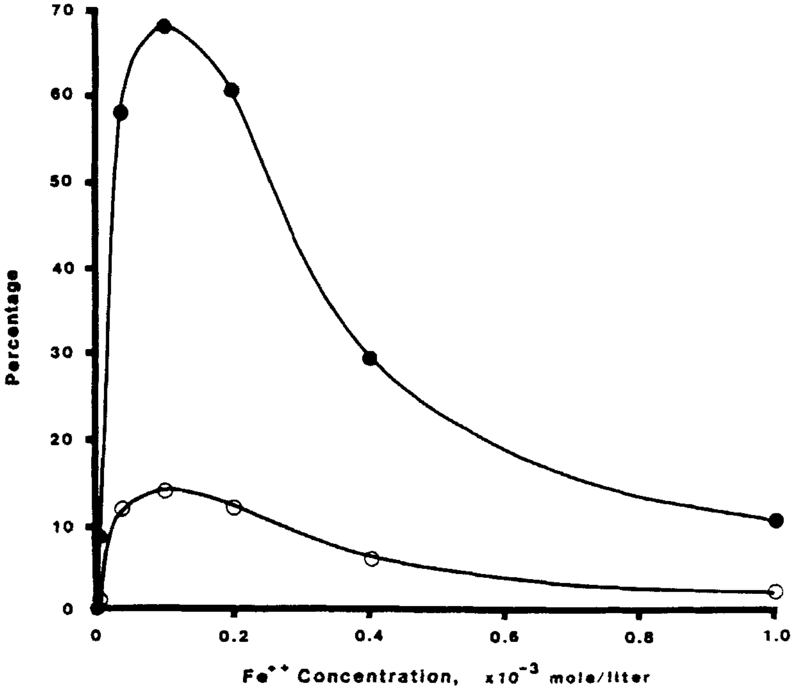


FIGURE 7. Effect of Fe^{2+} concentration on polymer load, % (black circles) and grafting efficiency, % (white circles) in grafting of PFA to cellulose. Reaction conditions are as in Figure 3.

through grafting (k_g), spontaneous decomposition (k_s), reaction of active centers with each other (k_b), or with hydroxyl radicals (k_h) on the other. This could be formulated as follows (PFA and cellulose being in excess and constant):

$$\frac{d\,(A.C.)}{dt} = k_f\,(HO^{\cdot}) - k_g\,(A.C.) - k_s\,(A.C.) - k_b\,(A.C.)^2 - k_h\,(A.C.)\,(HO^{\cdot}) \ldots \qquad (11)$$

The presence of the second order expressions connected with destruction of the active centers by pathways other than grafting

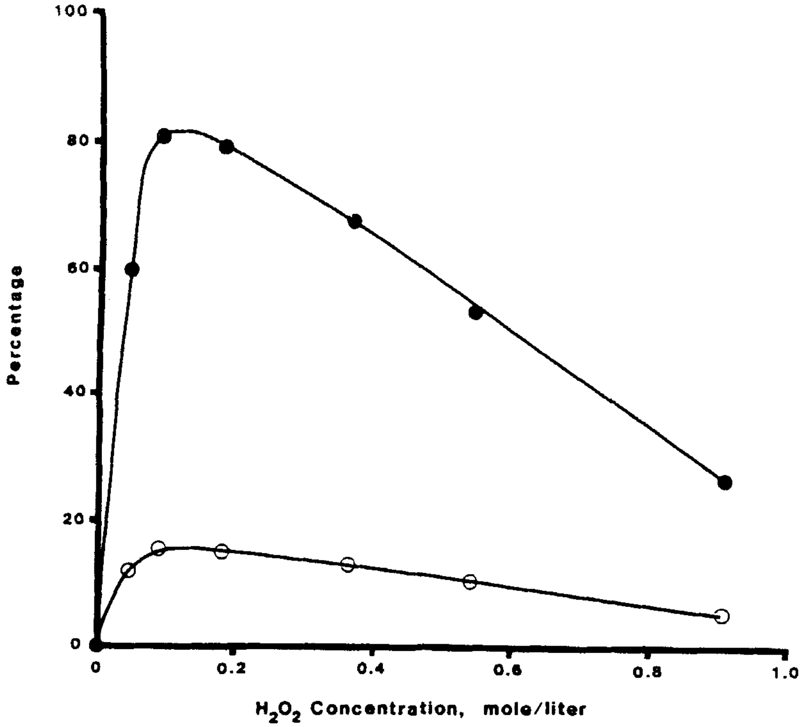


FIGURE 8. Effect of the concentration of H_2O_2/Fe^{2+} oxidant on polymer load, % (black circles) and grafting efficiency, % (white circles) in grafting of PFA to cellulose. Ratio of H_2O_2 to Fe^{2+} was 3.5×10^3 in moles. For other conditions see Figure 3.

would favor the grafting reaction at lower concentrations of hydroxyl radicals, while at higher concentrations the second order decompositions of the active centers should have a negative effect on grafting, with corresponding curves exhibiting a maximum. Similar relationships have been reported for other grafting systems.[20-25] Increased degradation of the grafted PFA at higher oxidant concentrations represents another possibility.[26]

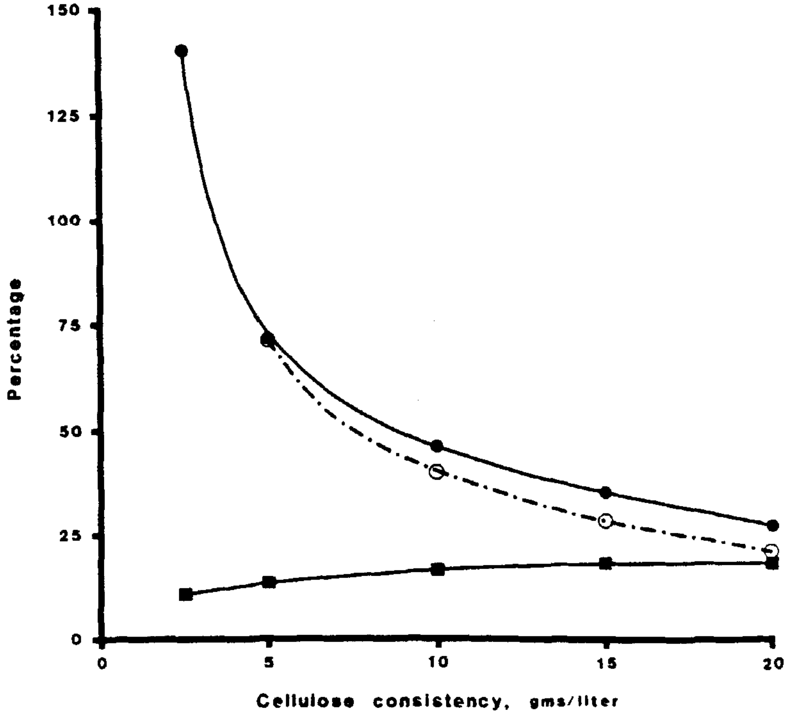


FIGURE 9. Effect of cellulose consistency on polymer load, % (black circles) and grafting efficiency, % (black squares) in grafting PFA to cellulose. For other conditions see Figure 3. White circles represent values calculated from the polymer load obtained at 2.5 g/l cellulose consistency assuming distribution of the same number of grafted PFA chains over the increasing amounts of cellulose used.

Influence of Cellulose Consistency on Polymer Load and Grafting Efficiency

Increase in the consistency of cellulosic fibers had a pronounced influence on the polymer load which dropped from 140% for the consistency of 2.5 g/liter to 27% for 20.0 g/liter. At the same time the grafting efficiency changed from 11.0% to 18.0% with the changes taking place mostly at the lower cellulose to PFA ratios (Figure 9). If we assume that grafting takes place by oxidative activation of PFA, the number of active centers formed in PFA should remain constant as the amounts of PFA and H_2O_2/Fe^{2+} reagent were kept constant throughout the experiments. As a result, with the increase in cellulose consistency the grafted PFA chains should become distributed over a larger number of cellulose fibers, the polymer load should go down, while grafting efficiency remain the same. The relationships obtained and the figures calculated from the polymer load at 2.5 g/liter cellulose consistency for the polymer loads at higher consistencies agreed reasonably well with the data experimentally obtained (Figure 9). Granted, the same relationships could also have been obtained by assuming cellulose activation and independence of the total number of active centers formed on cellulose from the molar ratio of H_2O_2/Fe^{2+} to cellulose repeat units; the latter is difficult to accept, however, in view of the relationships obtained earlier (Figure 8).

The preferential activation of PFA could also have resulted from occlusion of cellulosic fibers by PFA and exposure of PFA in preference to cellulose to the action of hydroxyl radicals generated in the aqueous medium; the experiments above thus do not necessarily indicate that cellulose cannot be oxidatively activated to graft to PFA, given a chance. Pretreatment of cellulose with H_2O_2/Fe^{2+} for 5 and 15 min. at 90°C (in either case all H_2O_2 was used up), followed by addition of PFA and 60 min. grafting at the same temperature resulted, however, in negligibly small polymer loads. This is in agreement with the experiments of Arthur et al,[27] who reported that the free radicals generated on cellulose by H_2O_2/Fe^{2+} had a very short lifetime becoming undetectable when the temperature was raised from -110°C to -60°C. Thus it appears that grafting of PFA to cellulose by cellulose activation, if possible, could take place only if two partners are simultaneously oxidized.

TABLE III.

Effect of Oxidative Pretreatment of PFA on the Polymer Load and Grafting Efficiency.*

PFA Pretreatment Time (minutes)	Apparent Polymer Load (%)	Apparent Grafting Efficiency (%)	Crosslinked PFA (%)	True Grafting Efficiency (%)
0	9.29	1.85	0.30	1.55
15	5.36	1.06	0.48	0.58
30	4.53	0.91	0.32	0.59

*For reaction conditions see experimental section. Apparent polymer load and apparent grafting efficiency are based on calculations including crosslinked PFA homopolymer into the grafting product.

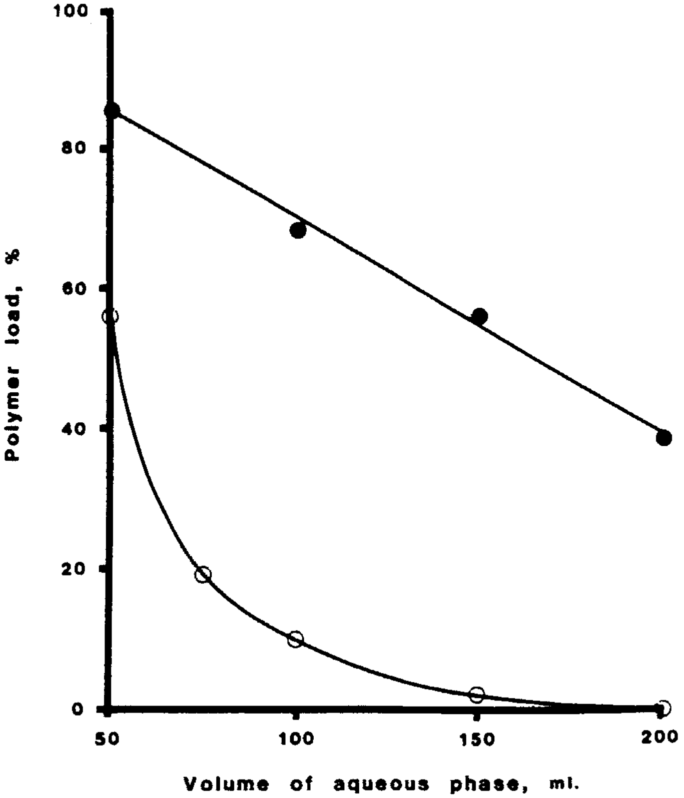


FIGURE 10. Effect of the volume of aqueous phase on polymer load in grafting PFA to cellulose. Black circles (0.01 x 10^{-3} mole Fe^{2+} used); white circles (0.1 x 10^{-3} mole Fe^{2+} used); H_2O_2 = 35.0 x 10^{-3} mole in either case. For other conditions see Figure 3.

Pretreatment of PFA with H_2O_2/Fe^{2+} at 90°C for 15 and 30 min. (in either case all H_2O_2 was used up) followed by addition of cellulose and grafting for 60 min. at 90°C gave the results summarized in Table 3. Correction for the insoluble, crosslinked polymer formed indicated that under the conditions used the true grafting efficiency at zero pretreatment time amounts to 1.55% vs. 0.58 and 0.59% after 15 and 30 min. pretreatment of PFA, respectively. Extrapolated to zero pretreatment time, the 15 and 30 min.

results suggest that under conditions generally used, the grafting of PFA involves formation of thermally stable, active functional groups to about 40%. The residual 60% of grafting involves formation of rather unstable active centers, either on PFA or on cellulose.

Effect of Volume of Aqueous Phase on Polymer Load and Grafting Efficiency

The increase in the volume of aqueous phase had a negative effect on the polymer load (Figure 10). The relationship was linear at the lower Fe^{2+} concentration, but was of a higher order at the higher Fe^{2+} concentration. The effect could be explained by the formation of hydroxyl radicals in aqueous medium and a smaller chance for them to react with the organic phase at higher dilutions. The higher order relationship obtained with the second curve suggests increased interaction between various oxidizing species in aqueous phase at higher Fe^{2+} concentration due to faster decomposition of H_2O_2 to hydroxyl radicals.

Effect of pH on Polymer Load and Grafting Efficiency

Figures 11 and 12 summarize the relationship between polymer load and pH of the aqueous phase for FA and PFA grafting. Since the oxidative activation reaction produces acidic species, the pH values of the aqueous phase at the beginning and the end of reaction differed appreciably in the higher pH region.

As mentioned before, crosslinking rather than grafting reaction is predominantly responsible for insolubilization of FA. With FA the apparent polymer load decreased with the increase in pH

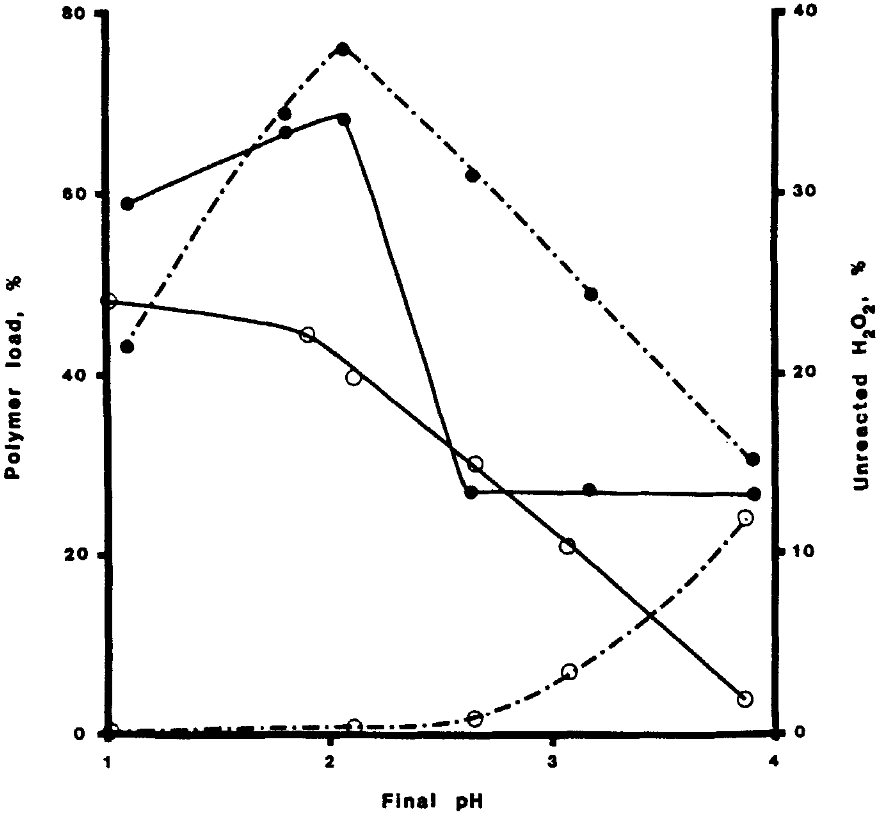


FIGURE 11. Relationship between final pH of the aqueous phase and polymer load in grafting PFA (black circles, solid line) or FA (white circles, solid line) to cellulose. In case of PFA the polymer load refers to material chemically attached to cellulose while in case of FA polymer load refers to crosslinked material not attached to cellulose as elaborated in the text. Black circles, dashed line refers to % of H_2O_2 remaining after PFA grafting while white circles, dashed line indicates the same for FA grafting. For other conditions see Figure 1.

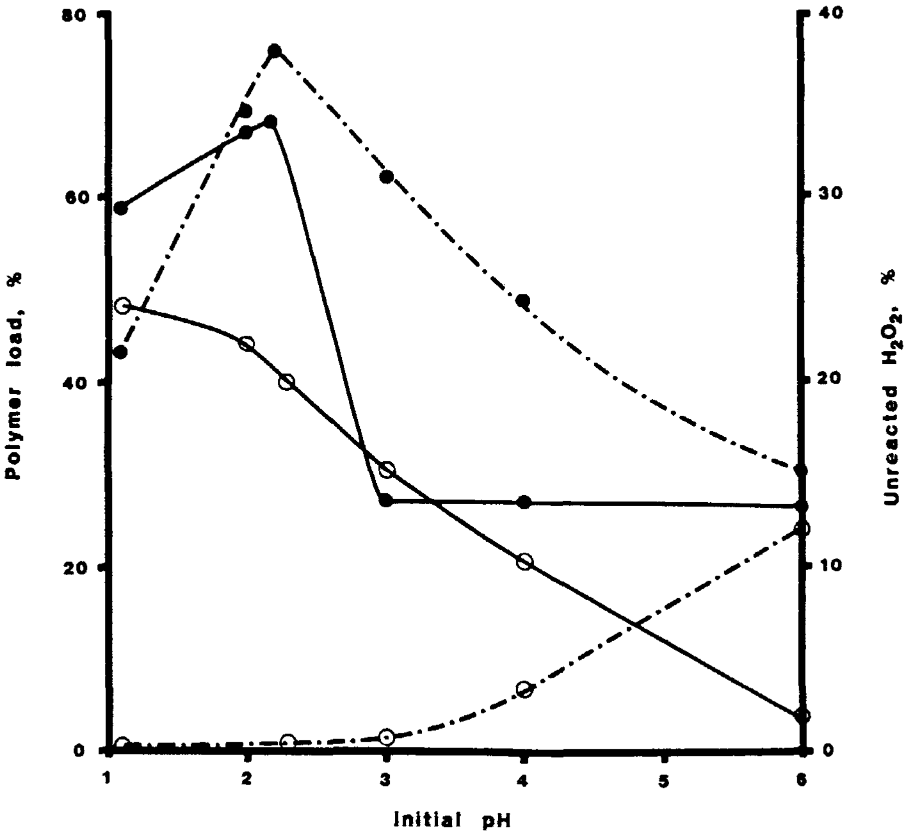


FIGURE 12. Relationship between initial pH of the aqueous phase and polymer load in grafting PFA and FA to cellulose. For symbols and conditions see Figure 11.

which is apparently due to a reduced rate of acidic polymerization and of acid-catalyzed crosslinking of the oxidatively activated materials. Incomplete usage of H_2O_2, possibly resulting from inactivation of the Fe^{2+} catalyst by precipitation as hydroxide at the higher pH values probably also contributed to the final result.

With PFA the insolubilization is primarily due to grafting. In this case the curve exhibited a maximum around pH 2.0, with the polymer load becoming practically independent of pH at the higher pH values. Interestingly enough the maximum in polymer load coincided with the minimum in H_2O_2 usage. Thus pH of about 2.0 represents the optimal value for utilization of H_2O_2 for grafting under the conditions used.

EXPERIMENTAL

Materials

Cellulose fibers were prepared by overnight soaking of the Whatman filter paper No. 1 in distilled water and defibration in a laboratory blender. The resulting slurry was filtered and the wet fibers (solids content: 19.17%) stored in plastic bags at 4°C. FA and PFA (Quacorr-1300) were obtained from Quaker Oats Co. FA was purified by fractional distillation at reduced pressure. Both, FA and PFA were stored at -15°C. H_2O_2 ("Perone" - 50% by weight) was supplied by E.I. DuPont de Nemours and Co.; $Fe(SO_4).(NH_4)_2 SO_4. 6H_2O$ and $HClO_4$ were commercial products used without purification.

Procedure

Grafting was carried out in a 250 ml three-neck round bottom flask fitted with a nitrogen inlet reaching below the surface of the liquid, thermometer, stirrer, and condenser. Cellulose fibers (about 0.5 g. O.D.) were suspended in 100 ml distilled water, pH adusted to 2.0 with perchloric acid, and the mixture brought to the desired temperature by immersion in a temperature controlled oil bath under stirring and nitrogen bubbling. Thereafter the Fe^{2+} catalyst was added, followed by FA or molten PFA, the mixture stirred for 1 min., and H_2O_2 added. The reaction time was counted from the addition of H_2O_2.

After the appropriate time period the reaction mixture was neutralized and cooled in ice. The resulting slurry was centrifuged for 1 hour at 900 rpm and the aqueous phase decanted. The organic part was treated with acetone, and centrifuged for 45 min.; the liquid portion was decanted and the remaining solids were Soxhlet extracted with acetone and water for 24 hours each time. The grafted fibers were dried to constant weight at 105°C. The grafting parameters were defined as follows:

$$\text{Polymer load (\%)} = (A-B)/B \times 100 \tag{12}$$

$$\text{Grafting efficiency (\%)} = (A-B)/C \times 100 \tag{13}$$

where, A = the weight of the O.D. products of graft copolymerization after solvent extractions; B = the weight of O.D. cellulose fibers before grafting; and C = the weight of FA or PFA used. When insoluble, crosslinked homopolymer was included in A-B, the above parameters were called apparent (vs true) polymer load, and grafting efficiency.

In determining the percent of crosslinking of FA, PFA, or of cellulose solubilization the same procedure was followed, except that the pertinent reaction partner was omitted.

Concentrations of H_2O_2 and Fe^{3+} were determined colorimetrically by $TiCl_4$ and tropolone procedures, respectively.[28,29] pH was determined at the ambient temperature using Beckman pH Meter, Model 3560.

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